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(54) **Process for preparing polyolefins with broad molecular-weight distribution.**

(57) A process for preparing polyolefins having a broad molecular-weight distribution with high stereoregularity and crystallinity. The process is adapted to polymerize olefins in the presence of a high activity catalyst. The process does not employ such a multi-stage polymerization method as employed in the prior art or two types of organic silicon compounds as in the prior art but uses only one selected from organic silicon compounds specified by a general formula $\text{Si}(\text{C}_6\text{H}_{11})_2(\text{OR})_2$ wherein C_6H_{11} is a cyclohexyl group and R is an alkyl group with 1 to 5 carbon atoms.

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BACKGROUND OF THE INVENTIONField Of The Invention

- 5 This invention relates to a process for preparing polyolefins, and more particularly to a process for preparing polyolefins with a broad molecular-weight distribution and excellent stereoregularity at high yields.

Background Of The Invention

- 10 A number of proposals have been made for the polymerization or copolymerization of olefins in the presence of a polymerizing catalyst comprising a solid catalyst component primarily consisting of titanium halides, a magnesium compound and an electron donor compound; an organic aluminum compound; a silicon compound; and the like. For Example, Japanese Patent Application Laid-Open Publication No. 3010/1988 (63-3010) assigned to the same assignee as the present application proposes an olefin
15 polymerization catalyst which comprises a solid catalyst component (A) prepared by contacting dialkoxymagnesium, a diester of an aromatic dicarboxylic acid, an aromatic hydrocarbon and titanium halides with one another to obtain a product and subsequently subjecting the product to a heating treatment in the powdered state; an organic aluminum compound (B); and an organic silicon compound (C). The Japanese patent provides examples directed to a process for polymerizing olefins in the presence of the catalyst.

- 20 Japanese Patent Application Laid-Open Publication No. 154705/1988 (63-154705) proposes an olefin polymerization catalyst which comprises a solid catalyst component (A), an organic aluminum compound (B) and a silicon compound (C) and provides examples directed to a process for polymerizing olefins in the presence of the catalyst. The catalyst component (A) for use in the catalyst is prepared by adding titanium tetrachloride to a mixed solution containing a magnesium compound obtained by reacting a magnesium
25 powder with alkylmonohalides in the presence of iodine, tetraalkoxy titanium, aliphatic hydrocarbon and aliphatic alcohol to precipitate a solid substance and adding a diester of phthalic acid thereto to obtain a solid product. The solid product is then brought into contact with titanium tetrachloride in the presence of aromatic hydrocarbon.

- Japanese Patent Application Laid-Open Publication No. 315406/1989 (1-315406) proposes an olefin
30 polymerization catalyst which comprises a solid catalyst component (A) prepared by forming a suspension of diethoxy magnesium and alkyl benzene, contacting the suspension with titanium tetrachloride and adding phthalic acid diester thereto to obtain a solid product which is recovered and washed with alkyl benzene. Subsequently the solid product is brought into contact with titanium tetrachloride in the presence of alkyl benzene, an organic aluminum compound, and an organic silicon compound to prepare the catalyst. The
35 Japanese patent also discloses examples directed to a process for polymerizing olefins in the presence of the catalyst.

- The foregoing catalysts exhibit a degree of activity sufficient to permit elimination the deashing which removes catalyst residues such as chlorine, titanium and the like remaining in a polymer produced, as well as to improve yields of a stereoregular polymer and increase the activity of the catalyst during polymeriza-
40 tion. While these catalysts have provided the foregoing benefits, the polyolefins obtained using these catalysts comprising the highly active catalyst component, organic aluminum compound and silicon compound have a narrow molecular-weight distribution as compared with polyolefins prepared by using the conventional olefin polymerizing catalyst which comprises the titanium trichloride based catalyst component, an organic aluminum compound and an electron donor compound which is added as required. The
45 narrowed molecular-weight distribution causes the formability or moldability of the polyolefin to deteriorate, resulting in some restrictions on the polyolefin's applications.

- Various approaches have been tried to improve the molecular weight distribution including the multi-stage polymerization process which provides polyolefins of increased molecular-weight distribution. However, the multi-stage polymerization requires a complicated polymerization operation repeatedly and
50 requires a troublesome treatment for recovering the chelating agent used during the polymerization, which increases the cost of the polymerization process.

- In view of the above, Japanese Patent Application Laid Open Publication No. 7703/1991 (3-7703) proposed a process for polymerizing olefins in the presence of an olefin polymerizing catalyst comprising a solid titanium catalyst component consisting essentially of magnesium, titanium, halogen and an electron
55 donor; an organic aluminum compound; and two types of organic silicon compounds serving as the electron donor. The Japanese patent states that the proposed polymerization process eliminates the need for the troublesome multi-stage polymerization process as described above and provides polyolefins of a molecular-weight increased to an intended degree. However, the proposed process likewise renders the

polymerization operation troublesome because it requires the use of two types of organic silicon compounds as the electron donor.

Accordingly, a need continues to exist for a polymerization process which produces polyolefins with a broad molecular weight distribution at high levels of catalyst activity.

SUMMARY OF THE INVENTION

The present invention has been made in view of the foregoing disadvantages of the prior techniques while, as a result of our study directed to development of a process for preparing polyolefins with broad molecular-weight distribution which is capable of simplified operation while permitting the catalyst to exhibit a high activity and providing a polymer with high stereoregularity and crystallinity, taking advantage of the fact that use of a specified organic silicon compound during the polymerization effectively eliminates the above described disadvantages of prior procedures.

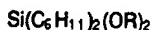
Accordingly, it is an object of the present invention to provide a process for preparing polyolefins with a broad molecular-weight distribution.

It is another object of the present invention to provide a process for preparing polyolefins which is capable of highly simplified operating procedures.

It is a further object of the present invention to provide a process for preparing polyolefins which is capable of ensuring increased polymerization activity.

It is still another object of the present invention to provide a process for preparing polyolefins with high stereoregularity and crystallinity.

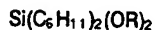
In accordance with the present invention, a process for preparing polyolefins with a broad molecular-weight distribution is provided. The process comprises the steps of subjecting olefins to polymerization or copolymerization in the presence of a catalyst comprising a solid catalyst component (A) primarily consisting of titanium halide, a magnesium compound and an electron donor compound; (B) an organic aluminum compound; and (C) an organic silicon compound, wherein the organic silicon compound (C) is represented by the following general formula:



wherein C_6H_{11} is a cyclohexyl group and R is an alkyl group having 1 to 5 carbon atoms.

DETAILED DESCRIPTION OF THE INVENTION

In the process for preparing polyolefins with a broad molecular-weight distribution according to the present invention, olefins are subject to polymerization or copolymerization in the presence of a catalyst comprising a solid catalyst component (A) mainly consisting of titanium halides, a magnesium compound and an electron donor compound; (B) an organic aluminum compound; and (C) an organic silicon compound, wherein the organic silicon compound (C) is represented by the following general formula:



wherein C_6H_{11} is a cyclohexyl group and R is an alkyl group having 1 to 5 carbon atoms.

The magnesium compound used in preparation of the solid catalyst component (A) is preferably dialkoxy magnesium including diethoxy magnesium, di-n-butoxy magnesium, diphenoxy magnesium, di-n-propoxy magnesium, di-sec-butoxy magnesium, di-tert-butoxy magnesium, diisopropoxy magnesium and the like. Diethoxy magnesium is most preferred.

In the preparation of the solid component (A) an aromatic hydrocarbon liquid at a normal (room) temperature is used as a solvent/suspension media. The preferred aromatic compound is selected from toluene, xylene, ethyl benzene, propylbenzen, trimethyl benzene and the like.

The electron donor used to prepare the solid catalyst component (A) is preferably an ester of aromatic carboxylic acid selected from a monoester of an aromatic carboxylic acid such as ethyl toluate, ethyl anisate, ethyl benzoate, methyl benzoate or the like and a diester of aromatic carboxylic acid including dimethyl phthalate, diethyl phthalate, diisopropyl phthalate, di-n-butyl phthalate, diisobutyl phthalate, di-n-amyl phthalate, diisoamyl phthalate, ethyl-n-butyl phthalate, ethylisobutyl phthalate, ethyl-n-propyl phthalate, diisooctyl phthalate, diisodecyl phthalate, diisopentyl phthalate, di-n-octyl phthalate, diisooheptyl phthalate or the like. Of the aromatic carboxyl esters, the diester of phthalic acid are preferred. Phthalic acid diesters having alkyl groups with 4 carbon atoms or less including diethyl phthalate, dimethyl phthalate, dibutyl

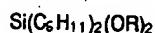
phthalate, dipropyl phthalate and the like and diesters of phthalic acid having alkyl groups with 5 carbon atoms or more including diisooctyl phthalate, diisodecyl phthalate, diisopentyl phthalate, di-n-octyl phthalate, diisohexyl phthalate and the like are particularly preferred.

As the solid catalyst component (A) may be used any suitable material so long as it contains a titanium halide, magnesium compound and electron donor. The solid catalyst component (A) may be prepared by using magnesium dichloride as the starting material and treating it together with titanium halide and the electron donor by grinding, dissolution and precipitation, spray drying, or the like. Alternatively, it may be prepared by using a dialkoxymagnesium as the starting material and contacting it with the titanium halide and electron donor.

More particularly, the solid catalyst component (A) may be prepared by forming a suspension of dialkoxymagnesium and aromatic hydrocarbon which is liquid at a normal temperature; adding titanium tetrachloride at a volume ratio of 1/2 or less to the aromatic hydrocarbon and an aromatic ester, preferably a phthalic acid diester, to the suspension to carry out a reaction therebetween at a temperature of from 80°C to 130°C to obtain a solid material; washing the solid material with aromatic hydrocarbon; and in the presence of aromatic hydrocarbon which is liquid at a normal temperature adding titanium tetrachloride at a volume ratio of 1/2 or less to the aromatic hydrocarbon to the solid material to carry out reaction therebetween at a temperature of from 80°C to 130°C, to obtain the solid catalyst component (A). Alternatively, the preparation may be carried out by preparing a mixture solution of aromatic hydrocarbon which is liquid at a normal temperature and titanium tetrachloride at a volume ratio of 1 or less; adding a suspension of spherical diethoxymagnesium, aromatic hydrocarbon which is liquid at a normal temperature and phthalic acid diester to the solution to carry out reaction therebetween at a temperature of from 80°C to 125°C, to thereby obtain a reaction product; washing the reaction product with aromatic hydrocarbon; and in the presence of aromatic hydrocarbon which is liquid at a normal temperature adding titanium tetrachloride at a volume ratio of 1 or less to the aromatic hydrocarbon to the reaction product to carry out reaction therebetween at a temperature of from 80°C to 125°C. The preparation may be also carried out by suspending dialkoxymagnesium in aromatic hydrocarbon to obtain a suspension; contacting the suspension with titanium tetrachloride at a volume ratio of 1 or less to aromatic hydrocarbon to obtain a reaction product; adding phthaloyl dichloride to the reaction product at a temperature of from 80°C to 125°C to carry out reaction therebetween, to thereby obtain a solid material; washing the solid material with aromatic hydrocarbon; and reacting the solid material in the presence of aromatic hydrocarbon with titanium tetrachloride at a volume ratio of 1 or less to the aromatic hydrocarbon therebetween at a temperature of from 80°C to 125°C, leading to preparation of the solid catalyst component (A). The solid catalyst component (A) may be also prepared by repeating three or four times the procedure comprising the steps of suspending dialkoxymagnesium in aromatic hydrocarbon to obtain a suspension; contacting the suspension with titanium tetrachloride at a volume ratio of 1 or less to the aromatic hydrocarbon to obtain a reaction product; adding phthaloyl dichloride to the reaction product at a temperature of from 80°C to 125°C to carry out reaction therebetween, to thereby obtain a solid material; washing the solid material with aromatic hydrocarbon; and reacting the solid material in the presence of aromatic hydrocarbon with titanium tetrachloride at a volume ratio of 1 or less to the aromatic hydrocarbon therebetween at a temperature of from 80°C to 125°C. Further, the solid catalyst component (A) may be prepared by forming a suspension of dialkoxymagnesium and aromatic hydrocarbon liquid at normal temperature; contacting the suspension with titanium tetrachloride; adding a phthalic acid diester having alkyl groups with 4 carbon atoms to the suspension at a temperature of 80°C or below; increasing temperature of the suspension; adding phthalic acid diester having alkyl groups with 5 carbon atoms or more to the suspension at a temperature of from 90°C to 110°C; further increasing the temperature of the reaction system to carry out reaction of the suspension at a temperature of from 90°C to 130°C to yield a solid composition; washing the composition with aromatic hydrocarbon; and adding titanium tetrachloride to the composition in the presence of aromatic hydrocarbon which is liquid at a normal temperature to carry out reaction therebetween at a temperature of from 80°C to 130°C, leading to production of the solid catalyst component (A). The above-described processes for preparation of the solid catalyst component (A) each are merely an example, therefore, the present invention is not limited to these processes.

The organic aluminum compound (B) used in the present invention includes trialkyl aluminum such as triethyl aluminum, triisobutyl aluminum or the like; alkyl aluminum halide such as diethyl aluminum chloride, ethyl aluminum sesquichloride or the like; and any combination or mixture thereof.

The organic silicon compound (C) used in the present invention is represented by the following general formula:



wherein C_6H_{11} is an cyclohexyl group and R is an alkyl group having 1 to 5 carbon atoms. More specifically, it is any one selected from the group consisting of dicyclohexyldimethoxy silane, dicyclohexyldiethoxy silane, dicyclohexyldipropoxy silane, dicyclohexyldibutoxy silane, and the like. Dicyclohexyldimethoxy silane is preferably used for this purpose.

Ratios among the components (A) to (C) used are not limited to any specific values so long as they do not deteriorate the advantages of the present invention. In general, the organic aluminum component (B) is used at a molar ratio of 5 to 1000 to the titanium atom content of the catalyst component (A) and the organic silicon compound (C) is used at a molar ratio of 0.002 to 0.5 to the organic aluminum component (B).

The polymerization may be carried out in the presence of or absence of an organic solvent. The olefin monomer used may be in the form of either gas or liquid. The temperature for the polymerization is generally 200°C or below and preferably 100°C or below. The pressure for the polymerization is generally $100\text{kg/cm}^2\text{G}$ or below and preferably $50\text{kg/cm}^2\text{G}$ or below.

Olefins which are subject to homopolymerization or copolymerization according to the present invention are preferably alpha olefins including ethylene, propylene, 1-butene, 4-methyl-1-pentene and the like.

In accordance with the present invention, only any one of the above-specified materials included in the organic silicon compound (C) is selected, so that polyolefins which have a broad molecular weight distribution sufficient to permit a numerical value obtained by dividing a weight-average molecular weight (M_w) by a number-average molecular weight (M_n) to be improved by 2 or more while keeping yields of a stereoregular polymer at a high level, as compared with polyolefins prepared according to the conventional process known in the art may be obtained with high yields.

Now, the present invention will be understood more readily with reference to the following examples and comparative examples, however, these are intended to illustrate the invention and are not to be construed to limit the scope of the invention.

Example 1

(Preparation of Solid Catalyst Component (A))

A round flask having an internal volume of 500ml and equipped with a stirrer was flushed with nitrogen gas. The flask was charged with 10g of diethoxy magnesium and 80ml of toluene to form a suspension. Then, 20ml of TiCl_4 was added to the suspension, the temperature was then gradually raised to 60°C . Then, 1.0ml of diethyl phthalate was added to the suspension, temperature was then gradually increased to 110°C . Subsequently, 2.5ml of diisooctyl phthalate was added to the suspension, which was further heated to a temperature of 112°C . A period of time as long as about 1.5 hours was required for heating the suspension to this temperature. Then, the temperature of the suspension was kept at 112°C , during which the suspension was reacted with the diethyl phthalate and diisooctyl phthalate for 1.5 hours, resulting in obtaining a reaction product. After the reaction was completed the reaction product was washed twice with 100ml of toluene (per wash) at 90°C and 20ml of TiCl_4 and 80ml of toluene were added to the reaction product, which was then heated to 100°C , to thereby carry out reaction therebetween for 2 hours while stirring. After the reaction, the resultant product was washed with 100ml of n-heptane at 40°C 10 times, resulting in a solid catalyst component being obtained. Solid and liquid materials in the solid catalyst component were separated from each other and then the solid material was subject to Ti analysis. The solid catalyst component contained 3.05% by weight of Ti.

(Preparation of Polymerization Catalyst and Polymerization)

An autoclave having an internal volume of 2.0 liters and equipped with a stirrer was flushed with nitrogen gas. The autoclave was charged with 1.32mmol of triethyl aluminum, 0.13mmol of dicyclohexyldimethoxy silane and 0.0066mmol of the solid catalyst component based on a Ti atom, to thereby prepare a polymerization catalyst. Then, the autoclave was charged with 1.8 liters of hydrogen gas and 1.4 liters of liquified propylene and the polymerization reaction performed for 30 minute at 70°C , resulting in a polymer of a weight (A) being produced. The resultant polymer was subject to extraction for 6 hours using boiling n-heptane to obtain a polymer of a weight (B) insoluble in n-heptane.

The polymerization activity (C) per gram of the solid catalyst component used is represented by the following expression:

(C) = (A)/(g)/amount of solid catalyst component (g)

A yield (D) of a total crystalline polymer is represented by the following expression:

$$(D) = (B)/(A) \times 100 (\%)$$

The values (A) to (D) obtained are listed on Table 1 together with an MI (E) of the polymer produced and its molecular-weight distribution (F).

Example 2

(Preparation of Solid Catalyst Component)

A round flask having an internal volume of 500ml and equipped with a stirrer was flushed with nitrogen gas. The flask was then charged with 10g of diethoxy magnesium and 80ml of toluene to form a suspension. Then, 20ml of $TiCl_4$ was added to the suspension, which was then heated to a temperature of 90°C. Then, 2.7ml of di-n-butyl phthalate was added to the suspension, the temperature was then increased to 115°C to carry out reaction therebetween for 2 hours while stirring, resulted in a solid reaction product. After the reaction was completed, the reaction product was washed with 100ml of toluene at 90°C twice and 20ml of $TiCl_4$ and 80ml of toluene were added to the reaction product, which was then heated to 115°C, to thereby carry out reaction therebetween for 2 hours while stirring. After the reaction, the resultant product was washed with 100ml of n-heptane at 40°C 10 times, resulting in a solid catalyst component being obtained. Solid and liquid materials in the solid catalyst component were separated from each other and then the solid material was subject to Ti analysis, which revealed that the solid catalyst component contained 2.61% by weight of Ti.

(Preparation of Polymerizing Catalyst and Polymerization)

The procedure in Example 1 was repeated except that the solid catalyst component prepared according to the above-described procedure in Example 2 was used. The results are shown in Table 1.

Example 3

(Preparation of Solid Catalyst Component)

1 liter stainless steel vibration mill was flushed with nitrogen gas and charged with 100g of magnesium dichloride and 24.5ml of di-n-butyl phthalate, which were subject to grinding for 20 hours. Then, the mill was charged with 200ml of toluene and grinding was further carried out for 3 hours, to thereby obtain a ground product. To the ground product, 1030ml of toluene and 48ml of toluene solution in which 6.9g of polystyrene was dissolved were mixed together with stirring, to thereby form a mixture. The resultant mixture was subject to spray drying using a CL-8 Type pin-type disc atomizer to obtain a dried product. 10g of the dried product is charged together with 100ml of $TiCl_4$ into a round flask equipped with a stirrer previously flushed with nitrogen gas, to form a suspension. Then, the suspension was gradually heated to 100°C, and held at that temperature for two hours to obtain a reaction product. After the reaction, the reaction system was cooled to 90°C and then supernatant liquid was removed from the reaction product. Thereafter, 100ml of $TiCl_4$ was added to the reaction system, which was gradually heated to 100°C, the reaction was carried out for 2 hours to obtain a product. The product was then washed with 100ml of n-heptane at 40°C 10 times to provide a solid catalytic component. The content of Ti in the solid catalytic component was 1.50% by weight.

(Preparation of Polymerization Catalyst and Polymerization)

The polymerization procedure described in Example 1 was repeated using the solid catalyst component prepared in accordance with Example 3. The results were shown in Table 1.

Example 4

(Preparation of Solid Catalyst component)

1 liter stainless steel vibration mill was flushed with nitrogen gas and charged with 30g of magnesium dichloride and 7.7ml of diethyl phthalate, which were then subject to grinding for 17 hours, to thereby obtain a ground product. Then, 10g of the ground product, 80ml of toluene and 20ml of TiCl_4 were charged into a round flask equipped with a stirrer previously flushed with nitrogen and then gradually heated to a temperature of 110°C , at which the charged materials were subject to reaction for 2 hours to obtain a reaction product. After the reaction, the product was washed with 100ml of n-heptane at 40°C ten times to obtain a solid catalyst component. The content of Ti in the resultant catalyst component was 2.22% by weight.

(Preparation of Polymerization Catalyst and Polymerization)

The procedure described in Example 1 was repeated using the solid catalyst component prepared above. The results were shown in Table 1.

Example 5

(Preparation of Solid Catalyst Component)

A round flask having an internal volume of 500ml and equipped with a stirrer was flushed with nitrogen gas. The flask was then charged with 30ml of toluene and 20ml of TiCl_4 , to thereby obtain a mixture solution. Then, a suspension formed of 10g of spherical diethoxy magnesium, 50ml of toluene and 3.6ml of di-n-butyl phthalate was added to the solution over 4 hours while the solution was kept at 20°C and the solution was raised to a temperature of 90°C , at which temperature the solution was subject to reaction for 1 hour while being stirred, to obtain a reaction product. After completion of the reaction, the resultant reaction product was washed with 100ml of boiling toluene twice and then 20ml of TiCl_4 and 80ml of toluene were added to the reaction product to carry out reaction therebetween at 110°C for 2 hours while being stirred, resulting in a reaction product. Subsequently, the product was washed with 200ml of n-heptane at 40°C ten times, leading to a solid catalyst component. The content of Ti in the solid catalyst component was 2.54% by weight.

(Preparation of Polymerization Catalyst and Polymerization)

The procedure described in Example 1 was repeated using the solid catalyst component prepared above. The results were shown in Table 1.

Example 6

(Preparation of Solid Catalyst Component)

A round flask having an internal volume of 500ml and equipped with a stirrer was flushed with nitrogen gas. The flask was then charged with 10g of diethoxy magnesium and 60ml of toluene to form a suspension. Then, 40ml of TiCl_4 was added to the suspension, which was then heated to a temperature of 80°C . Then, 2.0ml of phthaloyl dichloride was added to the suspension, the temperature was then increased to 115°C to carry out reaction therebetween for 2 hours while stirring, resulting in a reaction product. After completion of the reaction, the reaction product was washed with 200ml of toluene at 90°C twice and 60ml of toluene and 40ml of TiCl_4 were added to the reaction product, which was then heated to 115°C , and held at that temperature for 2 hours while stirring. After the reaction, the resulting product was washed with 200ml of n-heptane at 40°C 10 times, resulting in a solid catalyst component being obtained. The content of Ti in the resultant solid catalyst component was 3.59% by weight.

(Preparation of Polymerization Catalyst and Polymerization)

The procedure described in Example 1 was repeated using the solid catalyst component described above. The results were shown in Table 1.

Example 7

(Preparation of Solid Catalyst Component)

5 A round flask having an internal volume of 500ml and equipped with a stirrer was flushed with nitrogen gas. The flask was then charged with 10g of diethoxy magnesium and 60ml of toluene to form a suspension. Then, 40ml of $TiCl_4$ was added to the suspension, which was then heated to a temperature of $90^\circ C$. Then, 2.0ml of phthaloyl dichloride was added to suspension, of which a temperature was then increased to $115^\circ C$ to carry out reaction therebetween for 2 hours while stirring, resulting in a solid catalyst
 10 material. After completion of the reaction, the resultant material was washed with 200ml of toluene at a boiling temperature twice, and 60ml of toluene and 40ml of $TiCl_4$ were added to the material, which was then heated to $115^\circ C$, to thereby carry out reaction therebetween for 2 hours while stirring. This step was repeated three times, resulting in obtaining a reaction product. Thereafter, the reaction product was washed with 200ml of n-heptane at $40^\circ C$ 10 times, resulting in a solid catalyst component being obtained. A
 15 content of Ti in the resultant solid catalyst component was 2.00% by weight.

(Preparation of Polymerization Catalyst and Polymerization)

The procedure described in Example 1 was repeated that the solid catalyst component described
 20 above was used in an amount of 0.0033mmol based on a Ti atom for preparation of a polymerization catalyst. The results were as shown in Table 1.

Comparative Example 1

25 The procedures described in Example 2 was substantially repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced with phenyltriethoxy silane. The results were shown in Table 1.

Comparative Example 2

30 The procedure described in Example 2 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced with allyltriethoxy silane. The results were shown in Table 1.

Comparative Example 3

35 The procedure described in Example 4 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced with phenyltriethoxy silane. The results were shown in Table 1.

Comparative Example 4

40 The procedure described in Example 6 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced with phenyltriethoxy silane. The results were shown in Table 1.

Comparative Example 5

45 The procedure described on Example 7 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced with phenyltriethoxy silane. The results were as shown in Table 1.

Comparative Example 6

50 The procedure described in Example 1 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced by cyclohexylmethyldimethoxy silane. The results were shown in Table 2.

Comparative Example 7

55 The procedure described in Example 2 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced by cyclohexylmethyldimethoxy silane. The results were shown in Table 2.

Comparative Example 8

The procedure described in Example 3 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced by cyclohexylmethyldimethoxy silane. The results were shown in Table 2.

Comparative Example 9

The procedure described in Example 4 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced by cyclohexylmethyldimethoxy silane. The results were shown in Table 2.

Comparative Example 10

The procedure described in Example 5 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced by cyclohexylmethyldimethoxy silane. The results were shown in Table 2.

Comparative Example 11

The procedure described in Example 6 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced by cyclohexylmethyldimethoxy silane. The results were shown in Table 2.

Comparative Example 12

The procedure described in Example 7 was repeated except that dicyclohexyldimethoxy silane used for polymerization was replaced by cyclohexylmethyldimethoxy silane. The results were shown in Table 2.

As can be seen from the foregoing, polyolefins prepared according to the present invention have a molecular-weight distribution increased in value obtained by dividing a weight average molecular weight (M_w) by a number-average molecular weight (M_n) by at least 2 or more, as compared with polyolefins prepared by the prior art, resulting in being effectively directed to a wide variety of applications.

Also, polyolefins prepared by the present invention exhibit an increased polymerization activity based on a catalyst component and is increased in yield while being significantly improved in stereoregularity, to thereby exhibit much industrial utility.

Such advantages of the present invention are accomplished by the process of the present invention for polymerizing olefins in the presence of a catalyst of a high activity which does not employ multi-stage polymerization method or the method using two types of organic silicon compounds as described above in connection with the prior art but uses only one selected from the organic silicon compounds specified by the general formula $\text{Si}(\text{C}_6\text{H}_{11})_2(\text{OR})_2$ wherein C_6H_{11} is a cyclohexyl group and R is an alkyl group having 1 to 5 carbon atoms.

While the present invention has been described with a certain degree of particularity with reference to the examples, obvious modifications and variations are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described. general formula $\text{Si}(\text{C}_6\text{H}_{11})_2(\text{OR})_2$ wherein C_6H_{11} is a cyclohexyl group and R is an alkyl group having 1 to 5 carbon atoms.

While the present invention has been described with a certain degree of particularity with reference to the examples, obvious modifications and variations are possible in light of the above teachings. It is therefore to be understood that within the scope of the appended claims, the invention may be practiced otherwise than as specifically described.

Table 1

	Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Comparative Example 1	Comparative Example 2	Comparative Example 3	Comparative Example 4	Comparative Example 5
Total Amount of Polymer (A) g	233.2	278.6	210.8	148.1	267.6	193.7	442.8	284.6	192.6	141.0	202.5	454.5
Amount of Polymer Insoluble in Boiling n-Heptane (B) g	229.5	272.7	200.6	143.1	262.8	189.9	434.8	280.4	189.7	133.5	198.5	446.7
Polymerization Activity per Solid Catalytic Component (C) g/g	22.500	23.000	10.000	10.400	21.500	22.000	56.000	23.500	15.900	9.900	23.000	57.500
Yield of Total Crystalline Polymer (D) %	98.4	98.4	95.2	96.6	98.2	98.0	98.2	98.5	98.5	94.7	98.0	99.3
RI of Polymer Produced (E) g/10min	5.0	4.6	3.5	6.0	4.0	4.9	3.4	6.0	9.0	18.0	5.0	3.0
Molecular-Weight Distribution of Polymer Produced (F) (M_w/M_n)	7.8	6.0	7.7	6.0	6.2	6.1	6.2	4.0	4.0	3.9	4.0	3.9

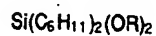
Table 2

	Comparative Example 6	Comparative Example 7	Comparative Example 8	Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12
Total amount of Polymer (A) g	280.9	359.8	225.5	165.2	342.3	273.9	575.4
Amount of Polymer Insoluble in Boiling n-Heptane (B) g	275.0	354.8	215.1	158.4	337.5	269.0	568.2
Polymerization Activity per Solid Catalytic Component (C) g/g	27.100	29.700	10.700	11.600	27.500	31.100	72.800
Yield of Total Crystalline Polymer (D) %	97.9	98.6	95.4	95.9	98.6	98.2	98.4
Mt of Polymer Produced (E) g/10min	5.1	6.5	2.4	12.2	8.0	5.5	5.0
Molecular-Weight Distribution of Polymer Produced (F) (M_w/M_n)	5.4	3.9	5.3	4.0	4.0	4.1	4.0

40 Claims

1. A process for preparing polyolefins with a broad molecular-weight distribution comprising the step of: subjecting olefins to polymerization or copolymerization in the presence of a catalyst consisting essentially of a solid catalyst component (A); an organic aluminum compound (B); and an organic silicon compound (C); wherein:

Said organic silicon compound (C) has the formula:



wherein C_6H_{11} is a cyclohexyl group and R is an alkyl group having 1 to 5 carbon atom.

2. The process of Claim 1, wherein said solid catalyst component (A) comprises titanium tetrachloride, magnesium dichloride and aromatic carboxylic acid ester.
3. The process of Claim 1, wherein said solid catalyst component (A) comprises titanium tetrachloride, dialkoxymagnesium and aromatic dicarboxylic acid diester.

4. The process of Claim 1 or 3, wherein said solid catalyst component (A) is prepared according to the procedure comprising the steps of:
 - preparing a suspension of dialkoxymagnesium and aromatic hydrocarbon which is liquid at a normal temperature;
 - 5 adding titanium tetrachloride at a volume ratio of 1/2 or less to said aromatic hydrocarbon and phthalic acid diester to said suspension to carry out reaction therebetween at a temperature of from 80°C to 130°C, to obtain a solid material;
 - washing said solid material with aromatic hydrocarbon; and
 - in the presence of aromatic hydrocarbon which is liquid at a normal temperature adding titanium
 - 10 tetrachloride at a volume ratio of 1/2 or less to said aromatic hydrocarbon to said solid material to carry out reaction therebetween at a temperature of from 80°C to 130°C, to thereby obtain said solid catalyst component (A).
5. The process of Claim 1, wherein said catalyst component (A) is prepared according to a procedure comprising the steps of:
 - 15 preparing a suspension by suspending dialkoxymagnesium in aromatic hydrocarbon which is liquid at a normal temperature;
 - contacting the suspension with titanium tetrachloride at a volume ratio of 1 or less to said aromatic hydrocarbon to carry out reaction therebetween to obtain a reaction product;
 - 20 adding phthaloyl dichloride to the reaction product at a temperature of from 80°C to 125°C to obtain a solid material;
 - washing the solid material with aromatic hydrocarbon; and
 - reacting said solid material in the presence of aromatic hydrocarbon with titanium tetrachloride at a volume ratio of 1 or less to the aromatic hydrocarbon therebetween at a temperature of from 80°C to
 - 25 125°C, to thereby obtain said solid catalyst component (A).
6. The process of Claim 1, wherein said catalyst component (A) is prepared according to a procedure comprising the steps of:
 - preparing a suspension by suspending dialkoxymagnesium in aromatic hydrocarbon;
 - 30 contacting the suspension with titanium tetrachloride at a volume ratio of 1 or less to said aromatic hydrocarbon to carry out reaction therebetween at a temperature of from 80°C to 125°C, to obtain a reaction product;
 - adding phthaloyl dichloride to the reaction product material;
 - washing the solid material with aromatic hydrocarbon; and
 - 35 reacting said solid material in the presence of aromatic hydrocarbon with titanium tetrachloride at a volume ratio of 1 or less to the aromatic hydrocarbon therebetween at a temperature of from 80°C to 125°C two to four times, to obtain said solid catalyst component (A).
7. The process of Claim 1 or 3, wherein said catalyst component (A) is prepared according to a procedure comprising the steps of:
 - 40 preparing a suspension of dialkoxymagnesium and aromatic hydrocarbon which is liquid at a normal temperature;
 - contacting the suspension with titanium tetrachloride;
 - adding phthalic acid diester having alkyl groups with 4 carbon atoms or less to the suspension at a
 - 45 temperature of 90°C or below increasing a temperature of the suspension and adding phthalic acid diester having alkyl groups with 5 carbon atoms or more to the suspension at a temperature of from 90°C to 110°C;
 - further increasing the temperature of the suspension to carry out reaction of the suspension at a temperature of from 90°C to 130°C, resulting in a solid composition being produced;
 - 50 washing the solid composition with aromatic hydrocarbon; and
 - adding titanium tetrachloride to the composition in the presence of aromatic hydrocarbon which is liquid at a normal temperature to carry out reaction therebetween at a temperature of from 80°C to 130°C, leading to production of said solid catalyst component.
- 55 8. The process of Claim 1 or 3, wherein said catalyst component (A) is prepared according to a procedure comprising the steps of:
 - preparing a mixture solution of aromatic hydrocarbon which is liquid at a normal temperature and titanium tetrachloride at a volume ratio of 1 or less to the aromatic hydrocarbon;

adding a suspension of spherical diethoxy magnesium, aromatic hydrocarbon which is liquid at a normal temperature and phthalic acid diester to said solution to carry out reaction therebetween at a temperature of from 80°C to 125°C, to thereby obtain a reaction product;

washing said reaction product with aromatic hydrocarbon; and

in the presence of aromatic hydrocarbon which is liquid at a normal temperature adding titanium tetrachloride at a volume ratio of 1 or less to said aromatic hydrocarbon to said reaction product to carry out reaction therebetween.

9. The process of one of Claims 1 to 8, wherein said organic silicon compound (C) is dicyclohexyldimethoxy silane.

10. The process of Claim 1, wherein the molecular weight distribution obtained by dividing a weight-average molecular weight (\overline{M}_w) by a number-average molecular weight (\overline{M}_n) is 6 or more.



European Patent
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EUROPEAN SEARCH REPORT

Application Number

EP 93 20 0923

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
X	EP-A-0 475 134 (TOSOH) * page 6, line 28 - line 38; claim 1; example 22 *	1,2,3,9, 10	C08F4/646 C08F10/00
X	EP-A-0 360 497 (MITSUI) * claim 1; examples 1,8 *	1,2,3,9, 10	
X	DE-A-4 114 833 (BASF) * page 3, line 64; claims 1,2 *	1,2,3,9, 10	
D,X	EP-A-0 385 765 (MITSUI) * page 9, line 11; claims *	1,2,3,9, 10	
			TECHNICAL FIELDS SEARCHED (Int. Cl.5)
			C08F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 23 JULY 1993	Examiner DE ROECK R.G.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		I : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons d : member of the same patent family, corresponding document	